

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets

(11)



EP 0 972 154 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
13.06.2001 Bulletin 2001/24

(51) Int Cl.7: **F16L 11/08, E21B 17/00**

(21) Application number: **98914418.3**

(86) International application number:
PCT/US98/06481

(22) Date of filing: **02.04.1998**

(87) International publication number:
WO 98/45635 (15.10.1998 Gazette 1998/41)

(54) COMPOSITE STRUCTURES HAVING HIGH CONTAINMENT STRENGTH

VERBUNDSTRUKTUREN MIT HOHER DRUCKBESTÄNDIGKEIT

STRUCTURES COMPOSITES A FORCE DE RETENTION ELEVEE

(84) Designated Contracting States:
AT BE DE FR GB NL PT

• MUELLER, Russell, R.
Washington, NJ 07882 (US)
• MARZINSKY, Cary, N.
Stockton, NJ 08559 (US)
• CHIU, Allen, S.
Florham Park, NJ 07932 (US)

(30) Priority: **04.04.1997 US 833157**

(74) Representative: Dew, Melvyn John et al
ExxonMobil Chemical Europe Inc.
Law Technology
P.O.Box 105
1830 Machelen (BE)

(43) Date of publication of application:
19.01.2000 Bulletin 2000/03

(73) Proprietor: ExxonMobil Research and
Engineering Company
Annandale, New Jersey 08801 (US)

(56) References cited:
EP-A- 0 024 512 BE-A- 825 080
DE-U- 8 805 593 GB-A- 2 165 331
US-A- 4 175 992

(72) Inventors:

- MONETTE, Liza M.
Whitehouse Station, NJ 08889 (US)
- ANDERSON, Michael, P.
Clinton, NJ 08809 (US)

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DescriptionBACKGROUND OF THE INVENTION5 Field of the Invention

[0001] The invention relates to pipes, tubing and containers having a wall structure composed of fiber reinforced polymer composites.

10 Description of Related Art

[0002] Fiber reinforced plastic (FRP) composites are finding increased usage as piping in chemical plants as well as casing used in the drilling of oil and gas wells and casing and tubing for the transport of crude oil and natural gas up from the well source. These materials are also useful in the construction of containers such as pressure vessels and underground or above ground storage tanks.

[0003] The advantage of FRP composites over carbon steel structures in oil/gas applications includes superior corrosion resistance, flexibility in achieving mechanical property design targets and improved fatigue resistance. FRP composites are also of considerably lighter weight for a given wall thickness than their steel counterparts.

[0004] FRP structures designed for use in high pressure piping or casing such as crude oil pipelines and oil well tubing are generally prepared by impregnating a roving of filaments of a high strength material, such as continuous glass filaments, with a thermosettable resin composition, such as an epoxy resin, and winding the impregnated filaments back and forth onto a mandrel under tension to form a plurality of intermeshed filament windings. Filaments may be wound at an angle of 90° to the pipe axis or at angles of 0° to less than +/- 90°, e.g., ± 88° with respect to the pipe axis, in which latter case a helical filament winding pattern is formed. After a desired pipe wall thickness is achieved, the winding operation is discontinued, the resin is cured and the mandrel is extracted resulting in a cylindrical pipe having a fiber reinforced wall structure. FRP pipes of this type and their method of production are disclosed, e.g., in U.S. Patents 2,843,153 and 5,330,807, the complete disclosures of which patents are incorporated herein by reference. Larger diameter structures such as containers may be fabricated the same way using larger diameter mandrels.

[0005] FRP pipe designed for use in onshore or offshore fossil fuel recovery must be constructed to withstand two basic forces to which it will be subjected. The first force is an outer radial load exerted along a vector normal to the pipe walls by fluids (oil or drilling muds) which are conveyed under moderate to high pressure through the pipe, also known as the hoop load. The second force is an axial tensile load exerted along vectors parallel to the pipe axis and occasioned by the weight of a long string of coupled pipe sections suspended in the ground at the well bore and/or between the well bore and surface platform in offshore recovery operations. These strings are often suspended 3,000 to 10,000 feet (about 850 to 2800 meters), and thus must be able to carry a long term axial stress in excess of about 2500 pounds per square inch (or 2.5 ksi) occasioned during operation and when the pipe string is inserted and removed during the fossil fuel recovery process. Other structures such as storage tanks and pressure vessels are designed primarily to maximize containment capability in a direction normal to the tank or vessel longitudinal axis, i.e., hoop load.

[0006] FRP pipe having maximum hoop strength can be designed if the reinforcing fiber is wound at an angle close to 90° to the pipe axis, e.g., +/- 70° up to 90°. Conversely, maximum tensile strength is developed where the reinforcing fiber is applied at an angle close to 0° to the pipe axis, e.g. +/- 30° down to 0°. However, pipe wound at or close to 90° exhibits severe diminishment of axial tensile strength while pipe wound at or close to 0° exhibits severe diminishment of hoop strength. Pipe wound at intermediate pipe axis angles between +/- 30° to +/- 70° (as disclosed in U.S. Patent 2,843,153) generally compromises hoop and particularly axial strength.

[0007] One technique for attempting to maximize both hoop and axial strength in pipe manufacture is to lay down the reinforcing fiber composite as separate laminate layers one atop another, each layer having the fibers disposed at different pipe axial angles designed to maximize the hoop or axial stress bearing properties of the pipe as well as minimize the coefficient of expansion of the composite pipe. An example of such a construction containing +/- 20° to +/- 60° fiber layers alternating with 90° layers is disclosed in U.S. Patent 5,330,807. Other similar layered laminates are disclosed in U.S. Patents 4,728,224 and 4,385,644.

[0008] FRP composites currently commercially available also may exhibit a serious deficiency which makes their use not cost effective in applications that generate even moderate containment stress. For example, microcracking and delamination of pipe wall structure at or near the pipe joints and/or along the pipe length provide a leak path for fluids, commonly referred to as "weeping", which can occur at fluid pressures which can be 5 to 10 times less than the pipe short-term burst pressure. Intrusion of water into the pipe wall structure via these microcracks can attack glass fiber surfaces and/or binder resin, leading to ply delamination of composite laminated structures and premature pipe failure. Other devices such as FRP underground storage tanks also exhibit premature microcracking and thus their corrosion resistance does not offer any additional advantages over similar metal structures.

[0009] Although microcracking can be mitigated by increasing the structural wall thickness, this solution drives the composite pipe cost up as compared to that of carbon steel structures. The higher cost constitutes a barrier to the substitution of FRP composite pipes for carbon steel in moderate to high (injection) pressure applications. Also, in downhole applications, the increased wall thickness prevents the use of composites where the diameter of the well bore is constrained, because of the cross-sectional area available for fluids to flow is smaller than that for carbon steel. The use of composites in these applications would require drill holes with larger diameter, and this gives rise to additional drilling costs.

[0010] Accordingly, it is a primary object of this invention to provide composite FRP structures having improved containment strength and which are more resistant to microcracking and delamination on the one hand and also have diminished wall thickness on the other hand such that the structure, e.g. pipe, is more compatible with carbon steel well bore/casing dimensions.

SUMMARY OF THE INVENTION

[0011] The invention provides a composite, fiber reinforced plastic structure having a wall portion defining a containment portion for the storage or passage of fluids or gases under high pressure, said wall portion comprising at least one layer comprising a plurality of continuous reinforcing fiberglass fibers having an average diameter of less than about 10 microns impregnated in a resinous binder.

[0012] In another embodiment of the invention, the fiber reinforced plastic structure is a pipe comprising an elongated hollow tubular body wherein the continuous fibers are disposed at an angle of 0° up to 90° with respect to the longitudinal pipe axis.

[0013] In a more preferred embodiment, the wall structure of the pipe comprises at least two fiber reinforced layers in fixed laminar contact, a first of said layers comprising continuous fiberglass fibers having an average diameter of less than about 10 microns impregnated in a resinous binder and disposed at an angle of 0° up to 90° with respect to the longitudinal pipe axis and said second layer containing continuous fiberglass fibers impregnated in a resinous binder and disposed at an angle with respect to the longitudinal pipe axis which differs from the angle of disposition of the fibers in said first layer.

[0014] Composite structures prepared in accordance with this invention exhibit an increased stiffness and containment strength in a direction normal to the reinforcing fiber axis due to the increased surface area of microfibers available for bonding to the resin matrix, as well as an improved resistance to microcracking after a prolonged period of use in the field. The composite structures also generally exhibit an increased longitudinal shear strength, also due to the increased surface area of microfibers available for bonding to the resin matrix.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] Figure 1 is an elevation view in partial section of one embodiment of a composite, laminated pipe element of this invention.

[0016] Figure 2 is a schematic drawing in cross section of another embodiment of a composite, laminated pipe element of this invention.

[0017] Figure 3 is a graph plotting composite transverse strength as a function of glass fiber diameter as predicted by microstructural mechanics computer model as compared to a measured value, for a fiber volume fraction of 60%.

[0018] Figure 4 is a graph showing short term failure envelope measured for a composite pipe having +/-55° disposed fiber and predictions from a theoretical computer methodology.

[0019] Figure 5 is a graph showing long term hoop design strength for a composite pipe having +/-55° disposed fiber subject to cyclic pressure at 200 cycles/min.

[0020] Figure 6 is a graph showing the long term failure envelope of conventional composite pipe having +/-55° disposed fibers having a diameter of 14 microns vs. pipe of the invention containing 7 micron diameter fibers.

DETAILED DESCRIPTION OF THE INVENTION

[0021] The invention relates to the utilization of micro-fibers (diameter less than 10µm) in polymer composite laminates such that the strength and longevity of pressure containing devices made from such laminates is increased in oil and gas production/transmission application. Pressure containing devices include: pipes, downhole tubulars, casing, pipelines, pressure vessels, underground storage tanks, composite wraps and like structures.

[0022] The example of glass fiber-reinforced composite pipe is shown below, where the containment pressure can be doubled (for fiber diameter of less than 4µm) from current commercially available levels. This is based on the fact the performance of pressure containing devices is limited by poor mechanical properties of the individual laminates, in the direction normal to the fiber axis. The modification involves substituting glass microfibers (diameter less than

10 μm) for glass fibers currently in use (diameter between 14 and 24 μm). This substitution is shown by microstructural mechanics computer methodology to increase stiffness and strength in the direction normal to the fiber axis, due to the increased surface area of microfibers available for bonding with the matrix. The use of micro-fibers therefore results in a substantial increase (up to a factor of two for fiber diameter of less than 4 μm) in device containment capability, particularly for downhole tubing and casing applications. Due to the greater surface area provided by micro-fibers, as compared to commercial fibers available for composite piping/tubing for oil/gas applications, a similar improvement (up to a factor of two) in composite shear properties is also realized, which is expected to lead to substantial increase (up to a factor of two) in device containment capability, particularly for surface and buried piping applications.

5 [0023] Two embodiments of the present invention where the pressure containing device is a pipe are shown in Figures 10 1 and 2. Figure 1 depicts a simple pipe construction of a two layer laminated pipe structure having an inner layer (a) comprising embedded fibers disposed at a 90° angle with respect to the longitudinal pipe axis in fixed contact with an outer layer (b) comprising embedded fibers disposed at a different angle, e.g. about +/-40° with respect to the longitudinal pipe axis.

15 [0024] Figure 2 depicts a laminated FRP pipe specifically designed to support the hoop and axial load stress forces 15 separately and is the subject matter of copending patent application [96CL058], filed in the United States Patent and Trademark Office on even date herewith.

20 [0025] In a preferred embodiment of the invention where a pipe wall structure comprises a single fiber reinforced 20 layer, the fiber may be disposed at an angle of 0° up to 90° more preferably from about +/-15° up to +/-75° with respect to the longitudinal pipe axis. Where the pipe wall comprises two or more fiber reinforced laminated layers as shown in Figs. 1 and 2, the fibers in one layer are preferably disposed at an angle of greater than +/-60° up to 90°, and the fibers in the adjacent layer are preferably disposed at an angle of greater than about +/-30° up to +/-60°, each with respect to the longitudinal pipe axis.

25 [0026] Figure 2 specifically shows an elevational view in partial section of a male threaded end section of pipe constructed in accordance with another embodiment of this invention. As shown, the pipe consists of an elongated hollow tubular body 1 constructed of three laminated fiber reinforced polymer layers shown at 2, 3 and 4 respectively and an optional fourth protective or wrapping layer shown at 5. The end section of the pipe shown at 6 comprises a male threaded tapered joint section cut or molded into outer reinforced layer 4. Reinforcing fibers shown forming helical patterns at 2 and 3 and a horizontal pattern at 4. The fiber patterns in Fig. 1 and Fig. 2, are drawn to illustrate fiber winding patterns and are not drawn to scale to show fiber winding density.

30 [0027] Layer 4 of Figure 2 is the axial load bearing layer of the pipe and is designed to bear substantially all of the axial load exerted on the pipe when a number of pipe segments are coupled to form strings and the string is disposed vertically under water and/or into well bores. Axial load is transmitted along layer 4 through female threaded connectors 30 or couplers (not shown) which are adapted to mate with two pipe ends which are to be joined during the construction of a pipe string. The taper and cut of male threaded joint section 6 extends into/onto axial load bearing layer 4, preferably to a degree short of reaching underlying layer 3.

35 [0028] The fibers present in binder layer 4 in Fig. 2 are disposed at an angle with respect to the longitudinal pipe axis designed to maximize the axial tensile load bearing properties of this layer, e.g., at an angle ranging from 0° up to +/-30°, more preferably up to about +/-15° and most preferably at about 0°. Fibers at 4 in Figure 2 are shown disposed at a 0° angle with respect to the pipe axis, but it is understood that this angle may vary up to and including +/- 30°.

40 [0029] Layer 3 shown in Figure 2 is a hoop load bearing layer of the pipe and comprises a second layer in fixed contact with layer 4 and is disposed radially inward of layer 4. The reinforcing fibers present in layer 3 are disposed at an angle of greater than +/-30° with respect to the longitudinal pipe axis, more preferably greater than +/-40° and up to 90° with respect to the pipe axis. Where layer 3 is the sole hoop load bearing layer, the fibers are preferably disposed at an angle of at least +/- 55°, more preferably about +/-70°, with respect to the pipe axis.

45 [0030] Layer 3 shown in Figure 2 may be the sole hoop load bearing layer or hoop stress may be further accommodated by one or more optional additional layers such as layer 2, which is disposed radially inward of layer 3 and in fixed contact therewith. Layer 2 contains reinforcing fibers disposed preferably at an angle greater than the angle of disposition of the fibers in layer 3 and up to an angle of 90° with respect to the longitudinal pipe axis. Most preferably the fibers in layer 2 are disposed at an angle of at least +/- 60° with respect to the pipe axis.

50 [0031] In a preferred embodiment of the invention where the pipe comprises three composite reinforcing layers, the fibers in layer 4 are disposed at an angle of about 0°, the fibers in layer 3 are disposed at an angle of +/- 40° to +/- 60° and preferably about +/- 55°, and the fibers in layer 2 are disposed at an angle of greater than +/-60°, preferably about +/-70°, each with respect to the longitudinal pipe axis.

55 [0032] Layer 5 shown in Figure 2 is an optional layer which may be applied as a protective layer or as a fiber reinforced winding layer to insure that the fibers in layer 4 are tightly bound in the resin binder. Layer 5 is not designed as an axial load bearing layer but may be simply a protective layer, and is cut away at the pipe ends prior to forming the tapered male threaded joint section 6.

[0033] Structures made in accordance with this invention may comprise a wall portion containing a single layer of

resin impregnated fibers, (layer a in Fig. 1 or layer 2 in Fig. 2), or two or more layers in fixed contact as depicted in Figs. 1 and 2.

[0034] The glass microfibers used in the present invention are extremely thin, having an average diameter of less than 10 microns, more preferably from about 3-9 microns, which distinguishes them from conventional glass fibers which have an average diameter of at least about 14 microns. Where the wall structure of the containment device comprises a single layer of resin impregnated fibers, the microfibers are used in that layer. Where the wall structure is a laminate of two or more different layers, the microfibers can be used in all layers or only in selected layers, with conventional glass or polymeric fibers being used in one or more other layers. Thus, in Fig. 1 layer (a) can comprise glass microfibers and layer (b) can comprise conventional glass fibers or other fibers such as graphite, aramide or Kevlar™ fibers. Similarly in Fig. 2 all of layers 2, 3, and 4 can comprise glass microfibers or only selected layers may comprise the glass microfibers.

[0035] Composite FRP structures of this invention e.g. pipes or cylinders, may be made by the well known wet filament winding process such as disclosed in the aforementioned U.S. Patent 2,843,153. By this method, a bundle of continuous reinforcing filaments is impregnated with a fluid resin melt or resin solution, preferably an uncured thermosetting resin, and fed under tension through a shuttle which traverses back and forth over a rotating mandrel. Alternatively, the rotating mandrel itself may traverse back and forth and the shuttle may be in a fixed position.

[0036] The impregnated fiber bundles are built up along the mandrel in close proximity or abutting one another and may form criss cross (helical) patterns as they are built up one layer atop another until the desired layer thickness is achieved. The angle of disposition of the fibers with respect to the mandrel longitudinal axis may be largely controlled as a function of the lateral speed of the shuttle as it traverses the mandrel. After the desired thickness of the initial layer is achieved e.g., layer (a) in Fig. 1 or layer 2 in Fig. 2, the lay down process is discontinued and the single layer structure is cured and removed from the mandrel. Where wall structures of two or more layer are to be made, the process is adjusted to lay down a second layer of resin impregnated fibers at an angle different than that of the initial layer, and so on. Axial load bearing layer 4 in Fig. 2 may also be applied using the filament winding technique except where the fibers are disposed at an angle of 0° with respect to the mandrel axis. In this latter case, the axial load bearing layer of desired thickness is applied as a resin saturated prepeg tape or sleeve which can be laid up by hand. Alternatively, a longitudinal lay down method may be used where 0° fibers are laid on the mandrel atop layer 3 while being captured by a 90° outer wrap, such as illustrated at 5 in Figure 2.

[0037] Other structures such as tanks and pressure vessels may also be made using the above filament winding process using a larger diameter mandrel, or by the lay up of resin fiber prepgs over a forming structure or mold.

[0038] The resinous material which serves as a binder for the reinforcing fibers is preferably a thermoset resin such as an epoxy. The preferred epoxy resins for carrying out the invention include bishpenol - A diglycidyl ester, bisphenol glycidyl ether, novolac resin glycidyl ether and aliphatic polyepoxide, though other suitable epoxy resins may be used. Aside from epoxy resins, other suitable thermosetting polymers include phenolic resins, unsaturated polyesters and polyimides. The degree of condensation of these resins is selected so that the viscosity of the resin product is adapted to the working conditions necessary for formation of the tubular body. The thermosetting polymers are mixed with suitable hardeners, such as aromatic polyamines, polyamides, aliphatic polyamines, polyacids, polyanhydrides, dicyandiamides, primary or secondary amines, mixtures of these, or any other of the hardeners typically used to crosslink thermosetting resins. Thermoplastic resins such as polyphenylene ethers, polysulfones, ABS resins and the like may also be used, but these are less preferred.

[0039] The quantity of resin applied to the glass microfibers in forming the structure should be sufficient such that the volume fraction of fiber present in the cured product is at least about 40%, more preferably at least about 50% and most preferably in the range of about 60 to 70%, with the balance being the resin composition.

[0040] The microglass or conventional glass reinforcing fibers used herein are supplied in the form of filaments or filament bundles. Most preferably, the individual fibers are coated with a material which will enhance the adhesion and wettability of the glass fiber surfaces with respect to the particular resin used as a binder. Aminopolysiloxane materials are particularly suited for this purpose.

[0041] After the resin-wetted composite structure is assembled on the mandrel, the thermosettable resin, e.g., epoxy resin, is cured by heating the structure to a temperature sufficient to cure the resin, e.g., 100° - 170°C, for a period of time ranging from about 30 minutes up to 12 hours, after which the assembly is removed from the mandrel. Thermoplastic resins need not be cured, but simply cooled on the mandrel prior to removal.

[0042] The wall thickness of composite FRP structures made in accordance with this invention may generally range from about 0.1 inch up to about 2.0 inches. Pipe diameters can range from about 1 to 36 inches. Common pipe dimensions consist of 4 inch inside diameter and 0.16 inch wall thickness. Common tubing dimensions comprise 2 inch inside diameter and .4 inch wall thickness. Where wall structures are made in accordance with this invention using two or more FRP laminated layers, it is preferred that the layer(s) containing the glass microfibers of this invention constitute at least 30% more preferably at least 50% of the overall wall thickness.

[0043] An epoxy resin binder material used in FRP pipe construction has a visco-elastic nature, and in consequence,

the piping/tubing mechanical properties such as strength decrease as a function of time. There exists well-established qualification procedures to determine the long term design (hoop) strength of a composite pipe. This involves subjecting a composite pipe to cyclic pressure (at 150° F), which is appropriate for applications with pressure less than or equal to 1000 psig, or to constant pressure, which is deemed appropriate for applications with pressure greater than 1000 psig. The hoop stress value at which loss of pipe containment integrity is observed is recorded. Data is extrapolated from a testing period of about one year to 10 or 20 year service, as needed. Conventional composite pressure containing devices subjected to this qualification procedure exhibit a long term (about 20 years) hoop design stress of 10 to 12 ksi for composite piping applications, and a long term axial and hoop design stress of 6 to 7 ksi for composite downhole tubing/casing applications.

[0044] In order to demonstrate the improved composite strength in a direction normal to the impregnated glass fibers, a pipe segment having reinforcing fibers disposed at a 90° angle with respect to the longitudinal pipe axis wherein the fibers have an average diameter of 7 microns was prepared by the winding process described above. A similar pipe containing conventional +/-55° wound fibers having an average fiber diameter of about 14 microns (current pipe) was also provided. Each pipe had a 60% glass volume fraction, 4 inch inside diameter and 0.16 inch wall thickness. A microstructural mechanics computer methodology is used to predict the laminate strength in the direction normal to the fiber axis as a function of fiber diameter. The model is validated by comparison with transverse composite strength value deduced from the +/-55 degree wound pipe with 14 μ diameter fibers (i.e. 11.2 ksi times sin² 55° = 7.5 ksi). Figure 3 shows the computer model predictions obtained for a typical epoxy matrix and a fiber volume fraction of 60%.

[0045] Figure 4 displays a measured short-term multi-axial failure envelop (open circles) for the +/-55° lay up composite pipe (epoxy Young's modulus of 430 ksi, and a tensile strength of 10 ksi) subjected to different petrochemical service conditions. 1. is for pure axial stress, 2. is for axial stress equal to hoop stress, 3. is for hoop stress twice the axial stress and 4. is for a pure hoop stress only. Conditions 1 and 2 are relevant to downhole applications (tubing, casing and injection tubing) while 3. is relevant to surface pipe and 4. to buried pipe applications respectively. Using a solid mechanics treatment incorporating the glass epoxy laminate properties directly measured from the 90 degree wound pipe (the laminate transverse and shear stress/strain curves) the short-term experimental failure envelope is matched with a 10% error by the results (full triangles) obtained by the above theoretical methodology.

[0046] In order to determine the long-term failure envelope, the long term design hoop strength of the above mentioned +/-55 degree wound pipe must be obtained according to qualification procedure API 15LR (cyclic service pressure less than 1000 psig), as depicted by Fig. 5. A pure pressure test is equivalent to loading condition 3 in Fig. 4. After extrapolation of the data to about a 20 year service life, the lower confidence level (LCL) of the long term hoop stress (LTHS) is about 10,000 psi, or 10 ksi. The long term composite transverse and shear strength are obtained by adjusting the composite strength parameters in the theoretical methodology until the predicted hoop strength for condition 3 is 10 ksi, as measured on Fig. 5. The long-term transverse composite strength is now 1.8 ksi, as compared to a short-term value of 7.5 ksi. Similarly, the long-term composite shear strength is 2.6 ksi, as compared to a short-term value of 10.7 ksi. The result from this procedure is shown in Fig. 6 (open circles). Condition 3. represents the experimentally measured data of Fig. 5, while the other conditions represent model predictions based on long-term composite properties derived from experimental point 3.

[0047] The projected performance of the invention is obtained by theoretically predicting the long-term failure envelope based upon the long term mechanical properties of a composite laminate made with a fiber whose diameter is 7 μ m. Figure 3 shows that the short term transverse composite strength of a pipe made with 7 μ m glass fiber is roughly 1.5 times greater than that of a composite laminate made with 14 μ m glass fiber. The assumption is that there is a similar short term composite shear strength increase. It is assumed that the long term 7 μ m glass fiber composite transverse and shear strength are also 1.5 times greater than conventional 14 μ m glass fiber composites. The reason is that the transverse Young's and shear modulus of a 7 μ m glass fiber composite are the same (or greater) than for a 14 μ m glass fiber composite. This implies that the fatigue behavior or creep rupture behavior of a micro fiber composite is the same (if not better) than that of conventional fiber composites. Fatigue behavior (cyclic loads) or creep rupture behavior (static loads) determines the magnitude of the long term composite strength. The long term predicted failure envelope for the invention is shown in Fig. 6 (full triangles). Points 1, 2 and 3 for the invention are 1.5 times greater than that of conventional 14 μ m fiber composite pipes, while point 4 is 1.2 times greater than that for the same conventional composites. Note that if the shear strength remains constant, point 3 for the invention is 40% greater, point 2,30% greater; point 1, 15% greater and point 4 is not increased as compared to conventional 14 μ m fiber composites.

[0048] The improvement in transverse composite strength of FRP pipe made in accordance with this invention is demonstrated in Example 1.

Example 1

[0049] Three different fiber reinforced composite pipes were constructed by the fiber winding process described above to provide pipe structures having a nominal 2 inch inside diameter and a nominal wall thickness of 0.1 inch.

Each pipe was wound at a 90° fiber angle with respect to the longitudinal pipe axis and contained a fiber volume fraction of about 46%. Pipe A, B and C were constructed using glass fibers having an average diameter of about 7, 14 and 24 μm , respectively. The relative composite transverse strength of each pipe was evaluated by clamping a segment of each sample in the jaws of an Instron™ testing machine and applying transverse (pulling) stress to the samples. The approximate stress and strain at break for each pip evaluated under identical test conditions was recorded and is shown in Table 1.

TABLE 1

Fiber Diameter (μm)	Stress at Break (psi)	Strain at Break (in/in)
A - 7	4.6×10^3	4.25×10^{-3}
B - 14	3.6×10^3	3.0×10^{-3}
C - 24	3.2×10^3	2.75×10^{-3}

As is evident from Table 1, the 7 μm fiber composite outperforms the 14 and 24 μm fiber composite by about 30 and 40%, respectively, which is in fair agreement with model predictions of about a 50% strength increase achieved with 7 vs. 14 μm fibers for a fiber volume fraction of 60% as shown in Figure 3.

Claims

1. A composite, fiber reinforced plastic structure having a wall portion defining a containment portion for the storage or passage of fluids or gases under high pressure, said wall portion comprising at least one layer comprising a plurality of continuous reinforcing fiberglass fibers having an average diameter of less than 10 microns impregnated in a resinous binder.
2. The structure of claim 1, wherein said fibers have an average diameter from 3 to 9 microns.
3. The structure of claim 1 or claim 2, wherein said structure is a pipe comprising an elongated hollow tubular body and wherein said continuous fibers are disposed at an angle of 0° up to 90° with respect to the longitudinal pipe axis.
4. The pipe structure of claim 3, wherein said continuous fibers are disposed to form a helical filament winding pattern forming an angle between about +/-15° up to about +/-75° with respect to said longitudinal pipe axis.
5. The structure of claim 1, wherein said fibers comprise at least 40% of the volume fraction of said wall portion.
6. The structure of claim 5, wherein said fibers comprise at least 60% of the volume fraction of said wall portion.
7. The pipe structure of claim 3, wherein said wall portion comprises at least two fiber reinforced layers in fixed laminar contact, a first of said layers comprising said continuous fiberglass fibers having an average diameter of less than 10 microns impregnated in a resinous binder and disposed at an angle of 0° up to 90° with respect to said longitudinal pipe axis and a second layer containing continuous fiberglass fibers impregnated in a resinous binder and disposed at an angle with respect to said longitudinal pipe axis which differs from the angle of disposition of said fibers in said first layer.
8. The pipe structure of claim 7, wherein the fibers in said first layer are disposed at an angle of greater than +/-60° up to 90° with respect to said longitudinal pipe axis and the fibers in said second layer are disposed at an angle of greater than about +/-30° up to +/-60° with respect to said longitudinal pipe axis.
9. The pipe structure of claim 7 or claim 8, wherein the fibers present in said second layer also have an average diameter of less than 10 microns.
10. The pipe structure of any one of claims 7 to 9, wherein said first layer of said pipe is an outer axial load-bearing layer.
11. The pipe structure of any one of claims 7 to 9, wherein said first layer of said pipe is an internal hoop load-bearing layer.

12. The structure of any preceding claims, wherein said resinous binder is a thermosetting resin, preferably an epoxy resin.

5 **Patentansprüche**

1. Faserverstärkte Verbundkunststoffstruktur mit einem Wandanteil, der einen Druckhüllenanteil zur Lagerung oder Hindurchleitung von Fluiden oder Gasen unter hohem Druck definiert, wobei der Wandanteil mindestens eine Schicht umfasst, die viele kontinuierliche verstärkende Glasfasern mit einem durchschnittlichen Durchmesser von weniger als 10 µm imprägniert in harzartigem Bindemittel umfasst.
2. Struktur nach Anspruch 1, bei der die Fasern einen durchschnittlichen Durchmesser von 3 bis 9 µm haben.
3. Struktur nach Anspruch 1 oder Anspruch 2, bei der die Struktur eine Leitung ist, die einen längeren hohlen röhrligen Körper umfasst, und wobei die kontinuierlichen Fasern in einem Winkel von 0° bis zu 90° in Bezug auf die Längsachse der Leitung angeordnet sind.
4. Leitungsstruktur nach Anspruch 3, bei der die kontinuierlichen Fasern so angeordnet sind, dass sie ein helixförmiges Filamentumwicklungsmuster bilden, das einen Winkel zwischen etwa ± 15° bis zu etwa ± 75° in Bezug auf die Längsachse der Leitung bildet.
5. Struktur nach Anspruch 1, bei der die Fasern mindestens 40 % der Volumenfraktion des Wandanteils umfassen.
6. Struktur nach Anspruch 5, bei der die Fasern mindestens 60 % der Volumenfraktion des Wandanteils umfassen.
7. Leitungsstruktur nach Anspruch 3, bei der der Wandanteil mindestens zwei faserverstärkte Schichten in festem Schichtverbundkontakt umfasst, wobei eine erste der Schichten die kontinuierlichen Glasfasern mit einem durchschnittlichen Durchmesser von weniger als 10 µm imprägniert in harzartigem Bindemittel und angeordnet in einem Winkel von 0° bis zu 90° in Bezug auf die Längsrichtung der Leitung umfasst, und eine zweite Schicht kontinuierliche Glasfasern imprägniert in harzartigem Bindemittel und angeordnet in einem Winkel in Bezug auf die Längsachse der Leitung enthält, der sich von dem Winkel der Anordnung der Fasern in der ersten Schicht unterscheidet.
8. Leitungsstruktur nach Anspruch 7, bei der die Fasern in der ersten Schicht in einem Winkel größer als ± 60° bis zu 90° in Bezug auf die Längsachse der Leitung angeordnet sind und die Fasern in der zweiten Schicht in einem Winkel von größer als etwa ± 30° bis zu ± 60° in Bezug zu der Längsachse der Leitung angeordnet sind.
9. Leitungsstruktur nach Anspruch 7 oder Anspruch 8, bei der die in der zweiten Schicht vorhandenen Fasern auch einen durchschnittlichen Durchmesser von weniger als 10 µm haben.
10. Leitungsstruktur nach einem der Ansprüche 7 bis 9, bei der die erste Schicht der Leitung eine äußere, Schublast tragende Schicht ist.
11. Leitungsstruktur nach einem der Ansprüche 7 bis 9, bei der die erste Schicht der Leitung eine innere, Umfangslast tragende Schicht ist.
12. Struktur nach einem der vorhergehenden Ansprüche, bei der das harzartige Bindemittel ein wärmehärtbares Harz, vorzugsweise Epoxyharz ist.

50 **Revendications**

1. Structure composite de matière plastique renforcée par des fibres ayant une partie de paroi définissant une partie de rétention pour le stockage ou le passage de fluides ou de gaz sous haute pression, ladite partie de paroi comprenant au moins une couche comprenant une pluralité de fibres de verre de renfort continues ayant un diamètre moyen inférieur à 10 micromètres imprégnées d'un liant résineux.
2. Structure selon la revendication 1, dans laquelle lesdites fibres ont un diamètre moyen de 3 à 9 micromètres.

3. Structure selon la revendication 1 ou 2, dans laquelle ladite structure est un tube comprenant un corps tubulaire creux allongé et dans laquelle lesdites fibres continues sont disposées selon un angle de 0 à 90° par rapport à l'axe longitudinal du tube.
5. Structure tubulaire selon la revendication 3, dans laquelle lesdites fibres continues sont disposées de manière à former un motif d'enroulement de filaments hélicoïdal formant un angle entre environ ± 15° et environ ± 75° par rapport audit axe longitudinal du tube.
10. Structure selon la revendication 1, dans laquelle lesdites fibres constituent au moins 40% de la fraction en volume de ladite partie de paroi.
15. Structure selon la revendication 5, dans laquelle lesdites fibres constituent au moins 60% de la fraction en volume de ladite partie de paroi.
20. 7. Structure tubulaire selon la revendication 3, dans laquelle ladite partie de paroi comprend au moins deux couches renforcées par des fibres en contact laminaire fixe, une première desdites couches comprenant lesdites fibres de verre continues ayant un diamètre moyen inférieur à 10 micromètres imprégnées d'un liant résineux et disposées selon un angle de 0° à 90° par rapport audit axe longitudinal du tube, et une deuxième couche contenant des fibres de verre continues imprégnées d'un liant résineux et disposées selon un angle par rapport audit axe longitudinal du tube qui diffère de l'angle formé par lesdites fibres de ladite première couche.
25. 8. Structure tubulaire selon la revendication 7, dans laquelle les fibres de ladite première couche sont disposées selon un angle supérieur à ± 60° et allant jusqu'à 90° par rapport audit axe longitudinal du tube et les fibres de ladite deuxième couche sont disposées selon un angle supérieur à environ ± 30° et allant jusqu'à ± 60° par rapport audit axe longitudinal du tube.
30. 9. Structure tubulaire selon la revendication 7 ou 8, dans laquelle les fibres présentes dans la deuxième couche ont également un diamètre moyen inférieur à 10 micromètres.
35. 10. Structure tubulaire selon l'une quelconque des revendications 7 à 9, dans laquelle ladite première couche dudit tube est une couche externe supportant la charge axiale.
11. Structure tubulaire selon l'une quelconque des revendications 7 à 9, dans laquelle ladite première couche dudit tube est une couche interne supportant la charge périphérique.
12. Structure selon l'une quelconque des revendications précédentes, dans laquelle ledit liant résineux est une résine thermodurcissable, de préférence une résine époxy.

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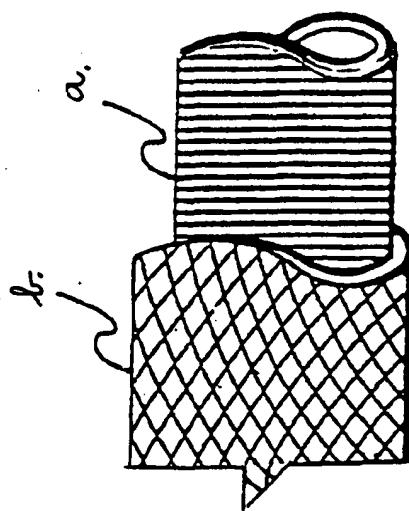
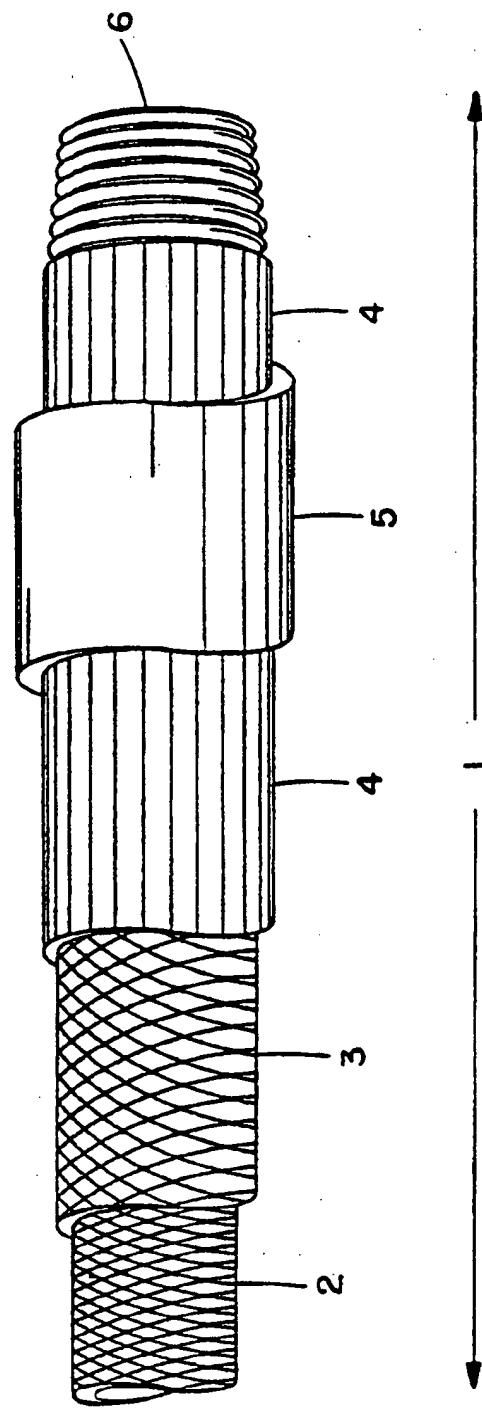


Fig. 1

FIG. 2



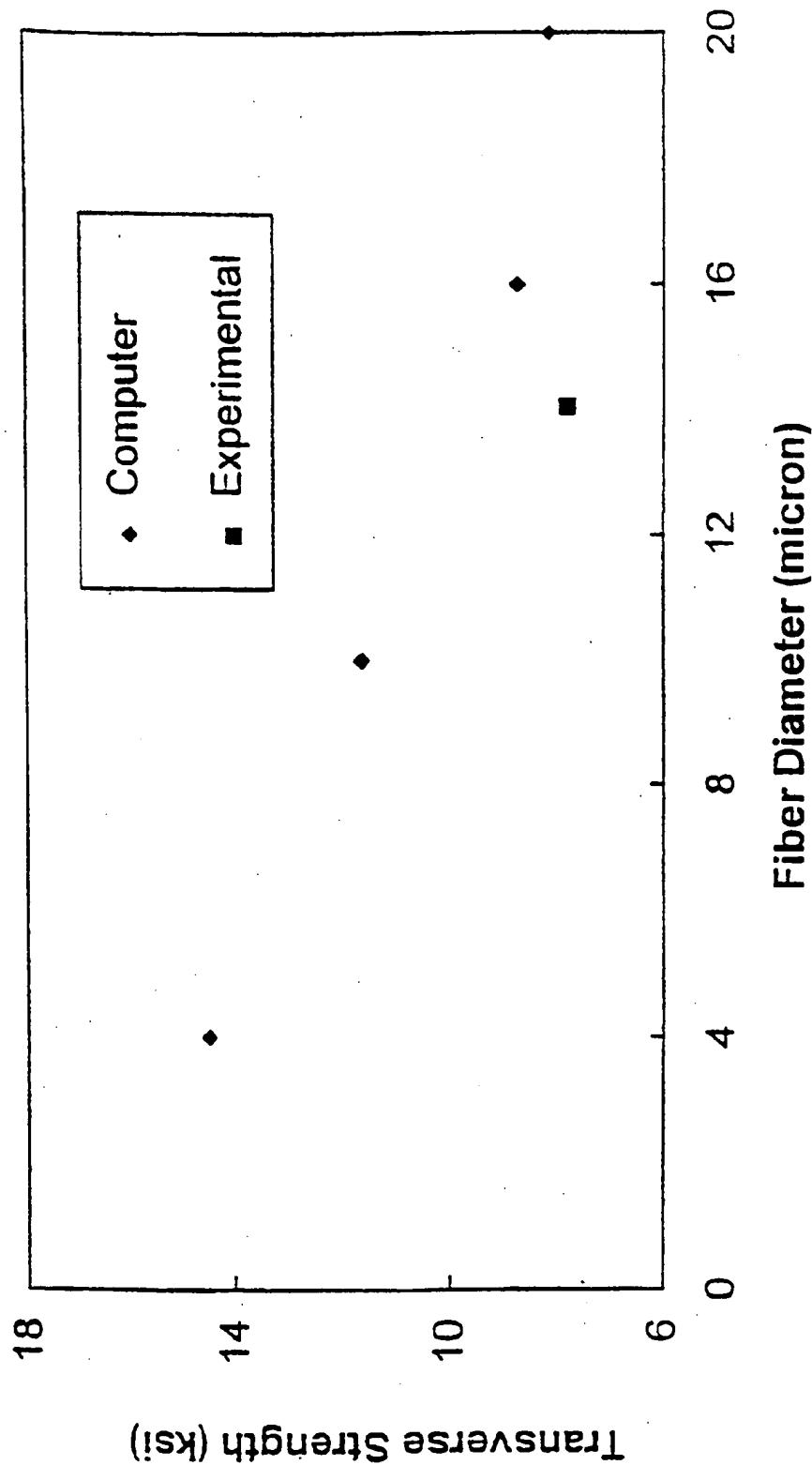


Fig. 3

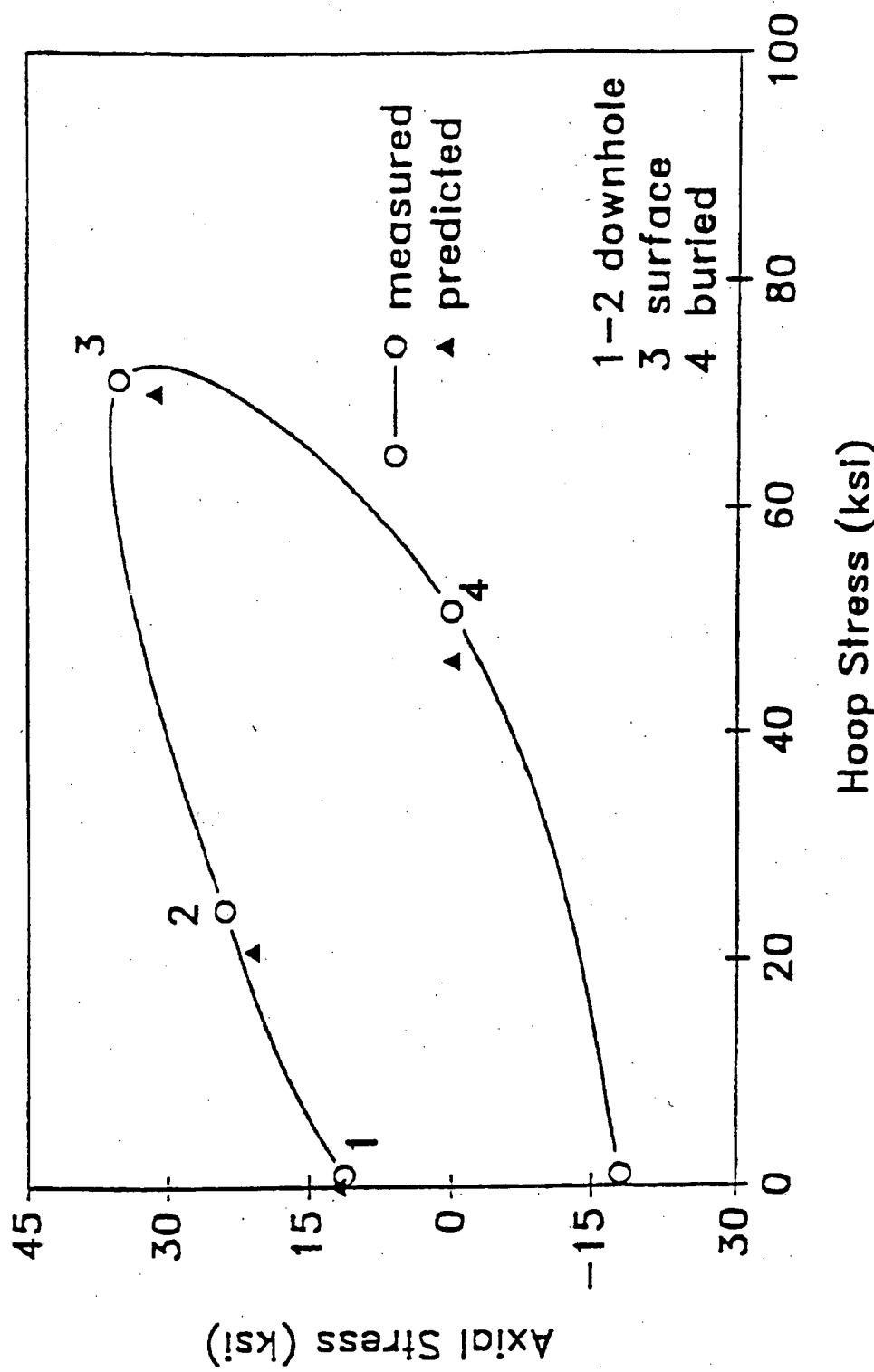


Fig 4

Viscoelasticity - Time Dependent Mechanical Properties
ASTM D2992 PROCEDURE B A (CYCLIC PRESSURE TEST)

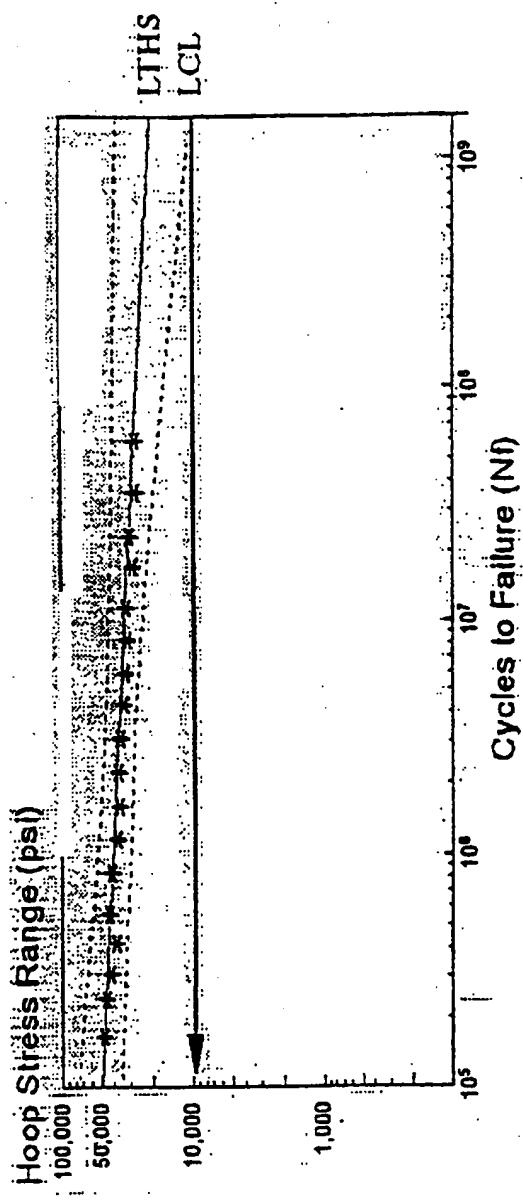


Fig. 5

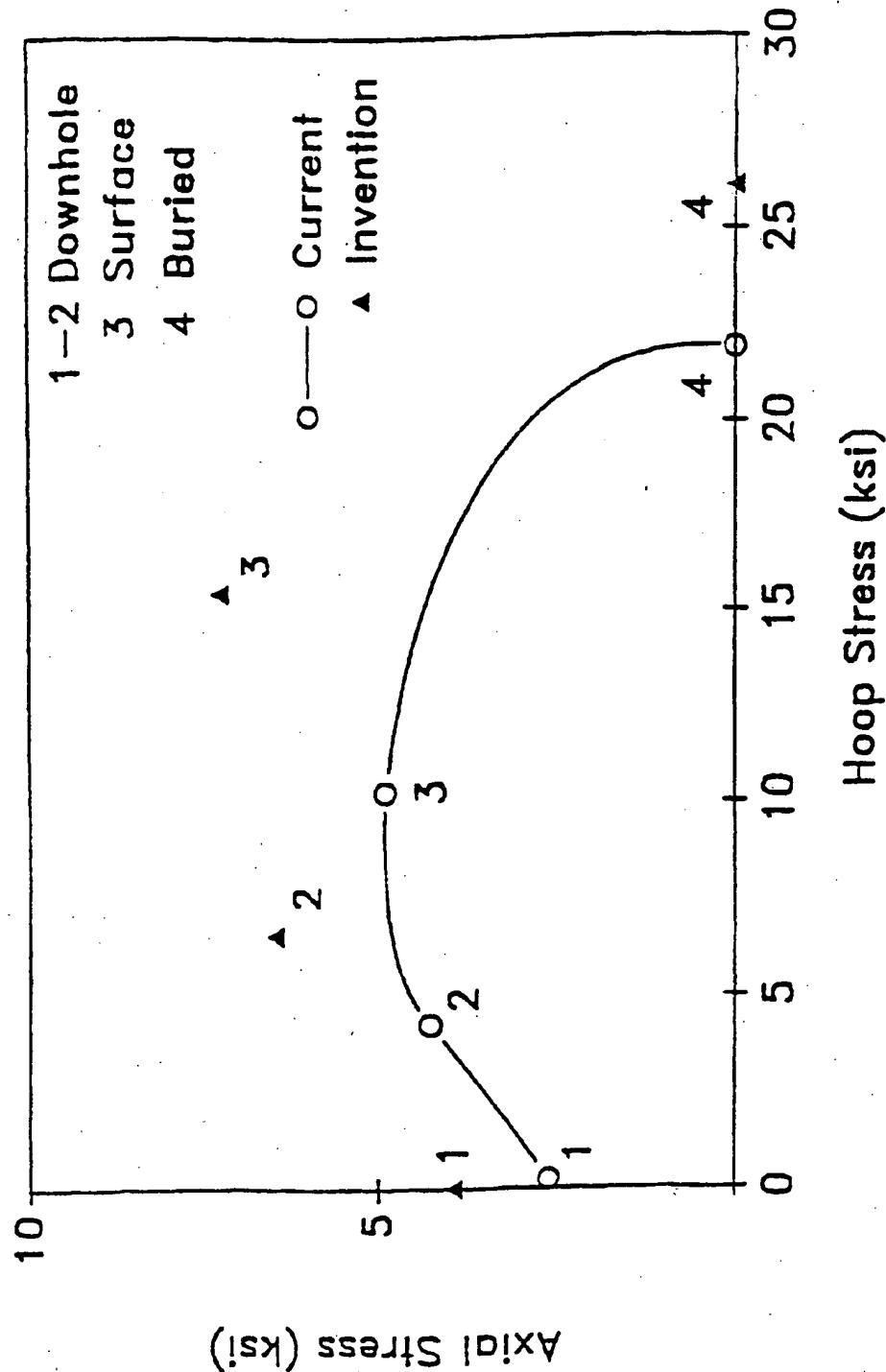


Fig. 6